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Kinetics and chemical equilibrium of the hydration of formaldehyde

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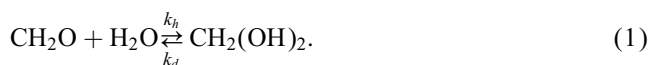
Abstract

The reaction rate of the hydration of formaldehyde is obtained from the measured, chemically enhanced absorption rate of formaldehyde gas into water in a stirred cell with a plane gas–liquid interface, and mathematically modelling of the transfer processes. Experiments were performed at the conditions prevailing in industrial formaldehyde absorbers, i.e. at temperatures of 293–333 K and at pH values between 5 and 7. The observed rate constants could be correlated as $k_h = 2.04 \times 10^5 \times e^{-2936/T} \text{ s}^{-1}$. Using the results, and the dehydration reaction rate constant, obtained previously at similar conditions, the chemical equilibrium constant for the hydration is obtained as $K_h = e^{3769/T - 5.494}$. © 2002 Elsevier Science Ltd. All rights reserved.

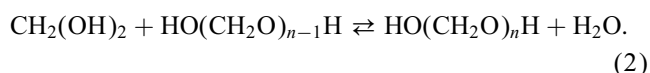
Keywords: Formaldehyde; Methylene glycol; Hydration; Kinetics; Chemical equilibrium; Absorption

1. Introduction

Formaldehyde is an important industrial intermediate in the manufacturing of resins, plastics, adhesives and many other products. Because formaldehyde is unstable in its pure, gaseous state it is usually produced as an aqueous solution. In such a solution, formaldehyde is almost completely hydrated to methylene glycol



Methylene glycol, in turn, depending on the strength of the solution, may polymerize to form a series of polyoxymethylene glycols



In the design of formaldehyde absorption and distillation processes, as well as in downstream processing, the kinetics and chemical equilibria of both reactions are important. The research group of Maurer recently studied the kinetics and

chemical equilibria of the polyoxymethylene glycol formation (Hasse & Maurer, 1991; Hahnenstein, Hasse, Kreidler, & Maurer, 1994b; Hahnenstein, Albert, Hasse, Kreidler, & Maurer, 1994a).

In the open literature, only two entries with experimental data on the reaction rate constant of the hydration of aqueous formaldehyde, k_h , were encountered. Schecker and Schulz (1969) obtained formaldehyde hydration rates from temperature jump experiments and measurement of the approach of the formaldehyde concentration to the new equilibrium value with UV-absorption. From experiments at 298–333 K they obtained $k_h = 7800 \times e^{-1913/T} \text{ s}^{-1}$ at pH = 4–7. Sutton and Downes (1972) obtained $k_h = 9.8 \text{ s}^{-1}$ at 295 K from radiolysis of aqueous solutions of methanol containing oxygen and semicarbazide hydrochloride in a flow system.

Most of the literature data on the chemical equilibrium constant of the hydration of formaldehyde, K_h , were obtained from the carbonyl specific UV-absorption at approximately 290 nm (Bieber & Trümpler, 1947; Ilceto, 1954; Landqvist, 1955; Gruen & McTigue, 1963; Siling & Axelrod, 1968; Schecker & Schulz, 1969; Zavitsas, Coffiner, Wiseman, & Zavitsas, 1970). At this wavelength an electron from a nonbonding oxygen n -orbital is promoted to an anti-bonding π^* -orbital of the carbonyl double bond (e.g. Calvert & Pitts, 1966). From their measurements mentioned above, Sutton and Downes (1972) could calculate also K_h at 295 K. Valenta (1960) used oscillographic polarography

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with pulses of short duration. Then, unhydrated formaldehyde is the only reducible species and its concentration could be obtained. Finally, Bryant and Thompson (1971) derived an expression for K_h from a consistent set of, partly experimental, thermochemical data. The values of K_h obtained by the various authors show a considerable spreading; differences of more than a factor 3 are found. The reaction enthalpy for the hydration obtained from the sources mentioned varies from -21.4 to -39.4 kJ mol $^{-1}$.

In previous work, K_h was usually determined from the concentrations of free formaldehyde and methylene glycol in aqueous solutions, i.e. from the equilibrium value of C_{MG}/C_F . We think that much of the spreading of the reported K_h data in the literature can be explained from the, occasionally unrecognized, complications in establishing these concentrations. In aqueous solutions, the concentration of unhydrated formaldehyde is very low because equilibrium (1) is far to the right. In addition, the molar extinction coefficient of formaldehyde in UV-absorption is small and its value for aqueous solutions is not known. In more concentrated solutions (say above 1 M) the amount of unhydrated formaldehyde is higher, but then the polymerization reactions (2) become significant and the methylene glycol concentration is not known anymore. Also, with more concentrated solutions, UV-absorption measurements are hampered by substantial nonspecific absorbance. Finally, commercial formaldehyde solutions often contain considerable amounts of methanol for stabilization; a fact that was not always recognized in older literature.

In this contribution, we report on the reaction rate of the hydration of formaldehyde, characterized by the rate constant k_h , at conditions prevailing in industrial formaldehyde absorbers, i.e. at temperatures of 293–333 K and at pH values between 5 and 7. Using these results, and the dehydration reaction rate constant, k_d , obtained previously at similar conditions (Winkelman, Ottens, & Beenackers, 2000), the chemical equilibrium constant for the hydration is obtained as $K_h = k_h/k_d$. The K_h data obtained this way, as the ratio of measured reaction rates rather than as the ratio of concentrations, are believed to be more reliable for the reasons mentioned in the section above.

The experimental technique for obtaining the hydration rate is based on the measurement of the chemically enhanced absorption rate of formaldehyde gas into water. In general, chemical enhancement occurs if the absorption of a gaseous component into a liquid is accompanied by a chemical reaction of that component in the liquid. If the reaction is fast enough, then the concentration of the component is reduced in the liquid already near the gas–liquid interface. This results in a larger gradient, and thus a larger flux, of the component, when compared to the gradient and flux without any reaction. The phenomenon is characterized by the so-called enhancement factor, E_i , which is defined as

$$E_i \equiv \frac{(J_i)_{x=0} \text{ with reaction}}{(J_i)_{x=0} \text{ without reaction}}, \quad (3)$$

where both fluxes at the gas–liquid interface, $(J_i)_{x=0}$, are based on the same concentration difference over the liquid film $(C_{i,\ell,IF} - \bar{C}_{i,\ell})$ (see, e.g. Chapter VII in Westerterp, Van Swaaij, & Beenackers, 1984).

Formaldehyde absorption experiments are carried out in a stirred cell reactor. The water in the reactor is stirred with a constant, but limited intensity, in such a way that the liquid surface always remains flat, and the value of the gas–liquid interfacial area remains accurately known. This way, the formaldehyde gas to liquid molar flux can be obtained from observed mass transfer rate, which, in turn, allows the calculation of the liquid phase chemical enhancement factor for formaldehyde mass transfer and the reaction rate of formaldehyde hydration, respectively, from mathematical modelling of the transfer processes.

The calculation of the desired hydration reaction rate from the observed mass transfer rate requires accurate knowledge of both the gas and liquid phase mass transfer coefficients. Therefore, prior to the kinetic measurements, the mass transfer coefficients prevailing in the stirred cell reactor were accurately measured.

2. Experimental

The experimental set-up for the kinetic measurements was build around a stirred cell reactor, see Fig. 1. The double walled glass reactor, 0.08 m diameter, 0.1 m height, was equipped with four baffles. Stirring was provided by a 0.046 m eight-bladed turbine stirrer in the gas phase, and a 0.050 m flat blade stirrer in the liquid phase on the same shaft, driven via a magnetic coupling. The liquid surface remained perfectly flat for stirring rates of up to 22 Hz. Beyond this limit, some rippling and heightening of water against the baffles was observed. Nitrogen was passed through a saturation column, approximately 1 m in height, filled with a 32 wt% aqueous formaldehyde solution, and flowed either via the head space of the reactor, or directly via a by-pass, to the analysis unit. The signals of the temperature control units, pressure measurement, flow measurement and stirring rate were stored into a computer. The composition of the

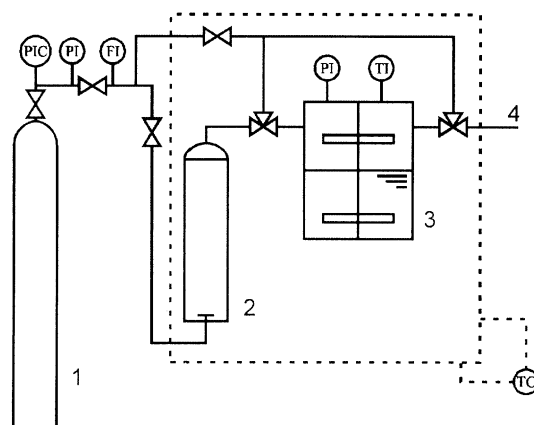


Fig. 1. Experimental set-up: (1) gas supply, (2) saturation column, (3) stirred cell and (4) to analysis unit.

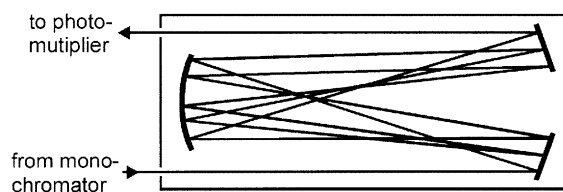


Fig. 2. Measuring cuvet for UV-absorption and optical path of the light.

solution in the saturation column was accurately determined using the sodium sulphite method (Walker, 1964).

The formaldehyde concentration of the gas stream entering and leaving the reactor were measured with UV-spectrophotometry using the carbonyl specific absorption around 295 nm. For this purpose, a special measuring unit was constructed by Macam Photometrics Ltd. UV-light was obtained from a low pressure deuterium discharge lamp with a stabilized power supply and reference intensity measurement for stable radiation output. Further, the unit was provided with collimating and alignment optics, a 2 nm band width monochromator, a special long-path measuring cuvet with temperature control, and a photomultiplier tube. The measuring cuvet, with a volume of only $40 \times 10^{-6} \text{ m}^3$, was equipped with two flat mirrors and a concave mirror, in such a way that a total optical path length of 1 m was achieved by 12 passes of the light through the cuvet, see Fig. 2. This way, the low extinction coefficient of the absorption band of gaseous formaldehyde was compensated for, and accurate measurements could be made.

In a typical kinetic experiment, the reactor was filled with the desired amount of distilled water, and the system, including the saturation column, the UV-absorption measuring cuvet, and all connections, was allowed to equilibrate to the desired temperature. Next, the nitrogen flow to the saturation column was set to the desired rate, and passed directly to the analysis unit, via the by-pass, to measure the reactor inlet formaldehyde concentration. The stirrer was switched to the desired rate, and the flow was led through the reactor until the achievement of a pseudo-steady state, as indicated by a constant UV-absorption reading from the spectrophotometer, marked the end of the experiment after a few minutes. This way, with an experiment, the hydration was measured at a single pseudo-steady-state point.

For the liquid phase mass transfer measurements, the gas supply was switched to CO_2 , and a vacuum pump was connected to the gas phase reactor outlet. Before an experiment, the water was degassed for 15 min by lowering the pressure to just above the water vapour pressure at the temperature employed. Next, the pressure was lowered even further, and the water allowed to boil for a short time, to drive out any gasses remaining. An experiment was started by pressurizing the reactor with CO_2 within a few seconds to approximately 0.12 MPa, closing the inlet valve, and recording the pressure decrease at a rate of exactly 1 Hz until the pressure decrease had diminished.

Gas phase mass transfer coefficients were obtained by measuring the evaporation rates of pure liquids into an

inert gas stream. For this purpose, a continuous N_2 , CO_2 or He gas supply was used, while the gas phase reactor outlet was now connected to three cold traps in series, cooled with liquid nitrogen, or, when CO_2 gas was used, a mixture of water, ice and CaCl_2 at approximately 258 K. A fourth trap, filled with CaCl_2 , prevented any moisture from the environment to enter. The amount of evaporated liquid was obtained from the weight increase of the cold traps. The following combinations of gases and pure liquids were used: N_2 with water, octane and ethanol; CO_2 with water; He with butyl ether, acetone, anhydrous propionic acid and butanol.

3. Results

3.1. Liquid phase mass transfer coefficients

The liquid phase mass transfer coefficients were determined by monitoring the pressure drop during the absorption of CO_2 in water, whilst operating both gas and liquid phases in batch mode. The variation of the CO_2 partial pressure with time, obtained from molar balances for CO_2 over both phases, is given by

$$\ln \left[\left(1 + \frac{V_g}{m_{\text{CO}_2} V_\ell} \right) \frac{P_{\text{CO}_2}}{P_{\text{CO}_2}^0} - \frac{V_g}{m_{\text{CO}_2} V_\ell} \right] = -k_\ell S \left(\frac{m_{\text{CO}_2} V_\ell}{V_g} + 1 \right) \frac{t}{V_\ell}, \quad (4)$$

where the distribution coefficient, m_{CO_2} , was taken from Versteeg and Van Swaaij (1988). Pressure readings were taken every second, for a total monitoring time varying from about half an hour to one hour. The individual experiments could be described by Eq. (4) very well: the mean absolute relative residual of the calculated and observed pressures never exceeded 0.1%.

The experimental k_ℓ -values were correlated using dimensionless groups, resulting in

$$Sh_\ell = 0.178 Re_\ell^{0.58} Sc_\ell^{0.36} \pm 4.5\%, \quad (5)$$

where a 4-fold variation of Sc and a 22-fold variation of Re were achieved by measuring at different temperatures and stirring rates, see Fig. 3.

3.2. Gas phase mass transfer coefficients

The gas phase mass transfer coefficients were obtained from the rate of evaporation of pure liquids into carrier gases. This way, any liquid side resistance against mass transfer was eliminated. The k_g values were calculated by solving, simultaneously, the balance equations for the vapour content of the carrier gas stream

$$k_{g,i} S (p_i^{\text{sat}} - p_i) = \frac{\phi_{v,g}^{\text{in}} P_i}{1 - P_i/P_{\text{tot}}} \quad (6)$$

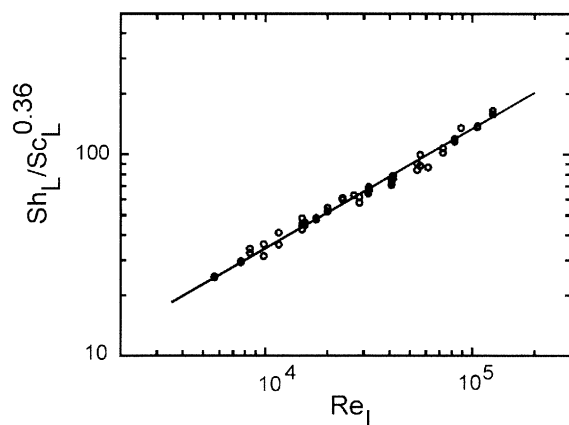


Fig. 3. Liquid phase mass transfer coefficients. (Symbols) Experimental data. (Line) Eq. (4).

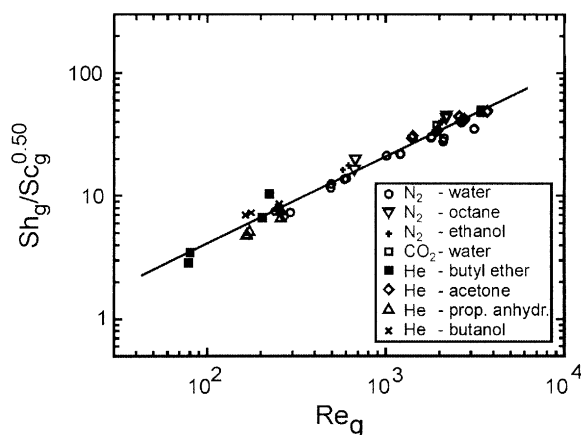


Fig. 4. Gas phase mass transfer coefficients. (Symbols) Experimental data. (Line) Eq. (7).

and the weight of condensed vapour accumulated in the cold traps

$$\frac{W}{M_{it}} = \frac{\phi_{v,g}^{in} P_i}{(1 - P_i/P_{tot})RT} \quad (7)$$

for $k_{g,i}$ and P_i . No influence of the gas flow rate on k_g was observed for any of the components. The k_g data were also correlated via dimensionless groups:

$$Sh_g = 0.163 Re_g^{0.70} Sc_g^{0.50} \pm 11\%. \quad (8)$$

By using eight combinations of carrier gases and liquids, and various stirring rates, a 23-fold variation of the Sc and a 50-fold variation of Re were achieved, see Fig. 4.

3.3. UV-analysis of formaldehyde

The formaldehyde concentration in the gas stream was obtained spectrophotometrically from the intensity of the characteristic absorption band of the carbonyl group at a wavelength of 295 nm. Simple aldehydes, p.e. acetaldehyde, propionaldehyde and butyraldehydes, show nearly

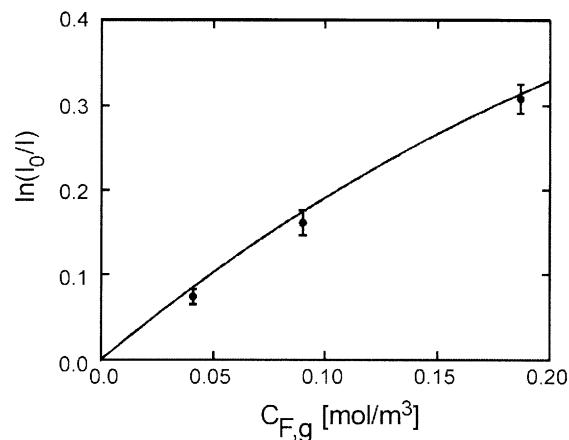


Fig. 5. Absorbance vs. gaseous formaldehyde concentration. (Symbols) This work, horizontal bars: standard deviation. (Line): Measured by Müller and Schurath (1983) at $C_{F,g} = 0\text{--}0.12 \text{ mol/m}^3$ and extrapolated to 0.2 mol/m^3 .

continuous absorption spectra in this wavelength region, and obey Beer's law (Calvert & Pitts, 1966; Müller & Schurath, 1983)

$$\ln(I_0/I) = \epsilon \ell C. \quad (9)$$

However, because of its simple structure, the absorption band of formaldehyde shows considerably more vibrational and rotational structure, and has a discrete line structure. Because the spectral line widths are narrower than the resolution of 2 nm used in the measurements, the absorbance varies nonlinear with the formaldehyde concentration. This has been reported previously by Moortgat, Seiler, and Warneck (1983), Müller and Schurath (1983) and Rogers (1990).

Müller and Schurath (1983) measured the absorption of gaseous formaldehyde in a 2.48 m cell in the concentration range of $0\text{--}0.12 \text{ mol m}^{-3}$. They correlated their results according to $\ln(I_0/I) = \ell C(2.186 - 2.702C)$. This correlation is illustrated in Fig. 5, together with our measured data, showing a good agreement. The gas phase formaldehyde concentrations of Fig. 5 are the ones in the gas stream entering the reactor, and are calculated from the composition of the solution in the saturation column, using the vapour–liquid equilibrium model of developed by the research group of Maurer (Maurer, 1986; Albert, García, Kuhnert, Peschla, & Maurer, 2000), and assuming that the gas leaving the saturation column has reached physical equilibrium with the liquid.

The absorbances vs. the formaldehyde gas concentrations for the entire concentration range employed here are shown in Fig. 6. They could be correlated with an expression similar to the one obtained by Müller and Schurath, and which is also shown in Fig. 6:

$$\ln(I_0/I) = \ell C(1.652 - 0.488C). \quad (10)$$

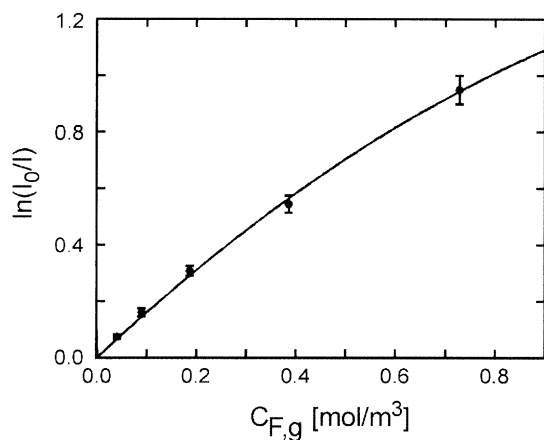
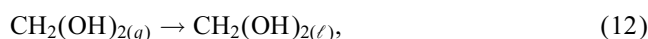


Fig. 6. Absorbance vs. gaseous formaldehyde concentration. (Symbols) This work, horizontal bars: standard deviation. (Line) Eq. (10).

3.4. Kinetic measurements

The gaseous phase above an aqueous formaldehyde solution contains formaldehyde gas, water vapour, and also methylene glycol vapour (Maurer, 1986). Therefore, the gas stream entering the stirred cell from the saturation column will contain these three components, and the absorption of formaldehyde in the reactor is accompanied by absorption of methylene glycol. Since the vapour pressure of water above an aqueous formaldehyde solution is lower than above pure water at the same temperature, some evaporation of water will also occur



Once absorbed, formaldehyde will be hydrated according to the reversible reaction (1). Since water is present in large excess, the hydration reaction can be characterised by a first-order rate constant, k_h (Bell, 1966).

$$R_F = k_h \left(C_{F,\ell} - \frac{C_{MG,\ell}}{K_h} \right). \quad (14)$$

The reaction rates of the polyoxymethylene glycol formation reactions, Eq. (2), are very low. Furthermore, if the overall concentration of formaldehyde is low (say below 1 wt%), the equilibrium constants of these reactions do not favour the formation of polyoxymethylene glycols and the solution will contain formaldehyde and methylene glycol. Therefore, any polyoxymethylene glycol formation is neglected in this work.

The experiments are evaluated using the two-film model. This model for mass transfer is based on the assumption that near the interface in the liquid phase a stagnant film exists, of thickness $\delta_\ell = D_\ell/k_\ell$, where any transport of the components is by diffusion only. Similarly, in the gas phase a film is present at the interface of a thickness $\delta_g = D_g/k_g$. Using

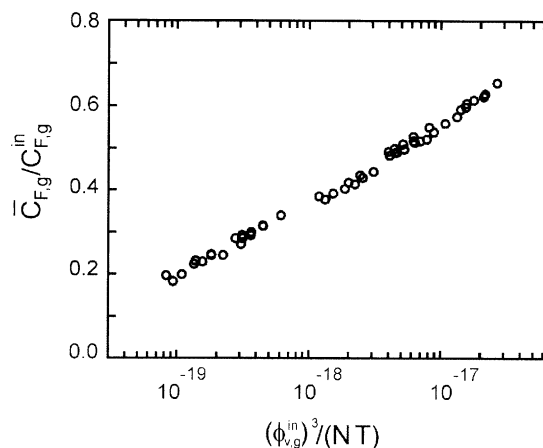


Fig. 7. Ratio of reactor outlet and inlet gas phase formaldehyde concentrations obtained experimentally.

the film model for mass transfer, the following equations describe the processes in the stirred cell

$$(J_i)_{x=0} S = \phi_{v,g}^{in} C_{i,g}^{in} - \phi_{v,g} \bar{C}_{i,g} \quad (i = F, MG, W, N_2), \quad (15)$$

$$(J_i)_{x=0} = k_{g,i} (\bar{C}_{i,g} - C_{i,\ell,IF}/m_i) \quad (i = F, MG, W), \quad (16)$$

$$(J_i)_{x=0} = k_{\ell,i} E_i (C_{i,\ell,IF} - \bar{C}_{i,\ell}) \quad (i = F, MG). \quad (17)$$

For the general case of absorption and/or desorption of two gases accompanied by a first-order reversible reaction in the liquid, Winkelman and Beenackers (1993) derived analytical solutions for the enhancement factors of the components involved. Translated to the notation used here, their equation for the enhancement factor of methylene glycol reads

$$E_{MG} = 1 + v(1 - E_F) \frac{C_{F,\ell,IF} - \bar{C}_{F,\ell}}{C_{MG,\ell,IF} - \bar{C}_{MG,\ell}}. \quad (18)$$

With the measured $\bar{C}_{F,g}$, and with $J_{N_2} = 0$ and $C_{W,\ell,IF} = \bar{C}_{W,\ell}$, the set of Eqs. (15)–(18) can be solved for the other gas phase concentrations, gas flow rate leaving the cell, interface concentrations, and mass transfer enhancement factors. In the calculations, it was assumed that the formaldehyde and methylene glycol concentrations in the bulk of the liquid are negligible compared to the interface concentrations, see Appendix A. The film thickness was obtained from Eq. (4) using $\delta_\ell = D_\ell/k_\ell$, and varied in the experiments from approximately 50–130 μm . The observed reactor outlet gas phase formaldehyde concentrations of the individual experiments increase with increasing gas flow rates, and decrease with increasing stirring rates and temperatures. In Fig. 7 the ratio of the reactor outlet and inlet formaldehyde concentrations is plotted vs. the quantity $(\phi_{v,g}^{in})^3/(N T)$, which was chosen intuitively for illustrative reasons only, to reduce the scattering of the data in the plot.

The enhancement factor of formaldehyde calculated from the experimental data can be equated to the one obtained from the differential equations for diffusion with parallel

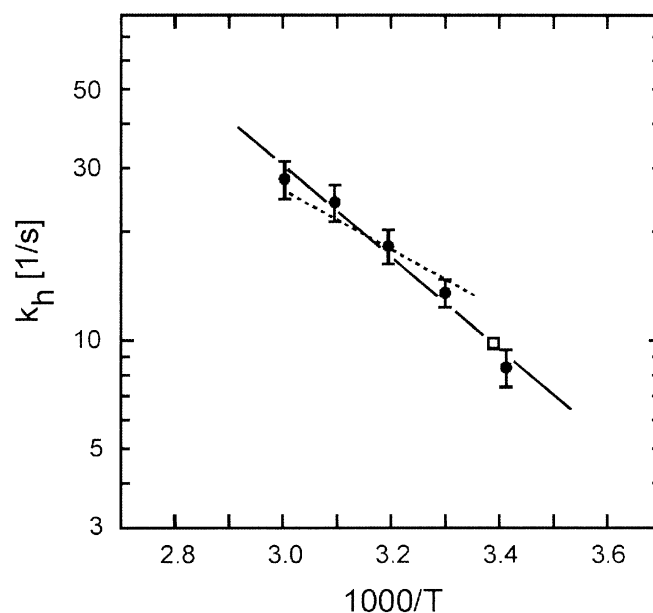


Fig. 8. Arrhenius plot of the formaldehyde hydration rate constant k_h . (Symbols) \bullet : This work, mean of 8–12 experiments, horizontal bars: standard deviation; \square : Sutton and Downes (1972). (Solid line) This work, Eq. (23). (Dashed line) Schecker and Schulz (1969).

reaction in the liquid according to the film model

$$D_{F,\ell} \frac{d^2 C_F}{dx^2} = k_h \left(C_F - \frac{C_{MG}}{K_h} \right) \quad (0 \leq x \leq \delta_\ell), \quad (19)$$

$$D_{MG,\ell} \frac{d^2 C_{MG}}{dx^2} = -k_h \left(C_F - \frac{C_{MG}}{K_h} \right) \quad (0 \leq x \leq \delta_\ell). \quad (20)$$

An analytical solution of Eqs. (19) and (20) for the E_F , with the assumption of negligible liquid bulk phase concentrations, reads (Winkelman & Beenackers, 1993)

$$E_F = 1 + \frac{\left(\frac{\phi_R}{\tanh[\phi_R]} - 1 \right) \left(K_h - \frac{C_{MG,\ell,IF}}{C_{F,\ell,IF}} \right)}{K_h + v}, \quad (21)$$

where the reaction factor, ϕ_R , is defined by

$$\phi_R = \delta_\ell \sqrt{\frac{k_h(K_h + v)}{D_F K_h}}. \quad (22)$$

With the values of E_F obtained from Eqs. (15)–(18), the reaction rate constants, k_h , were calculated numerically from Eqs. (21) and (22), where the equilibrium constant K_h was written as $K_h = k_h/k_d$, and k_d was taken from Winkelman and Beenackers (2000). The values of ϕ_R obtained numerically ranged from 3.7 to 11.4.

Finally, regression of the reaction rate constants with the reciprocal temperature gave

$$k_h = 2.04 \times 10^5 \times \exp\left(\frac{-2936}{T}\right) \text{ s}^{-1}. \quad (23)$$

The mean absolute relative deviation between the data from the individual experiments and from Eq. (23) is 9.6%, see Fig. 8. From the temperature coefficient the activation energy

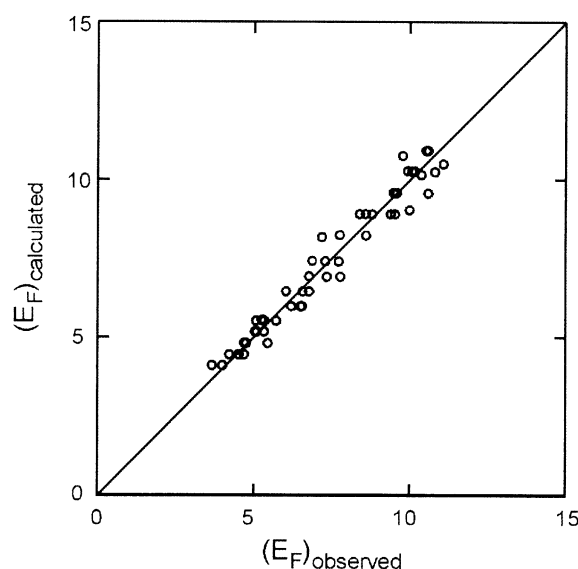


Fig. 9. Parity plot of the formaldehyde enhancement factors.

was found as $E_a = (24.4 \pm 2.7) \text{ kJ mol}^{-1}$. Regression of the results according to the transition-state theory resulted in $\Delta H^\ddagger = (21.8 \pm 2.7) \text{ kJ mol}^{-1}$ and $\Delta S^\ddagger = (-152.0 \pm 9.5) \text{ J mol}^{-1} \text{ K}^{-1}$. The enhancement factors obtained from Eqs. (21)–(23) are plotted against the ones obtained from the experimental data and Eqs. (15)–(18) in Fig. 9.

With the hydration rate according to Eq. (23), and the dehydration rate obtained previously (Winkelman & Beenackers, 2000) the equilibrium constant for the hydration of

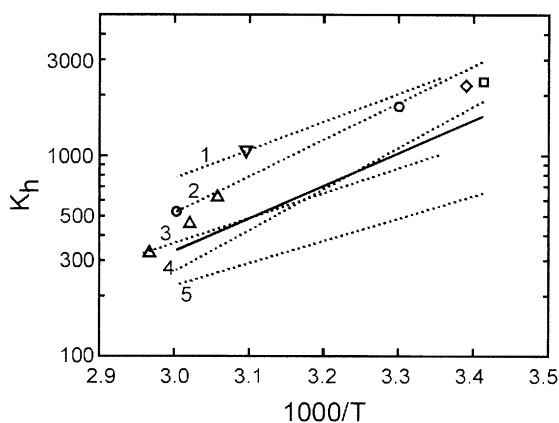


Fig. 10. Van 't Hoff plot of the formaldehyde hydration chemical equilibrium constant. (Solid line) This work, Eq. (24). (Symbols) ∇ : Landqvist (1955); Δ : Bieber & Trümpler (1947); \square : Valenta (1960); \circ : Iliceto (1954); \diamond : Sutton and Downes (1972). (Dashed lines) 1: Schecker and Schulz (1969); 2: Zavitsas et al. (1970); 3: Gruen and McTigue (1963); 4: Bryant and Thompson (1971); 5: Siling and Akselrod (1968).

formaldehyde can be obtained as

$$K_h = \frac{k_h}{k_d} = \exp\left(\frac{3769}{T} - 5.494\right). \quad (24)$$

Eq. (24) is illustrated in Fig. 10. From the temperature coefficient in Eq. (24) the reaction enthalpy of the hydration was obtained as $\Delta H = -31.4 \text{ kJ mol}^{-1}$.

4. Discussion

The relation for the liquid phase mass transfer coefficients, Eq. (5) is of a form often encountered in the literature. Usually, the exponent of Sc_ℓ is taken as 1/3 based on theoretical reasons (Westerterp, et al., 1984). The exponent of 0.36, obtained from fitting the data, is in good agreement with this theoretical value. The value of the exponent of Re_ℓ obtained here, 0.58, is at the lower end of the wide range encountered in the literature for this type of reactor: from 0.5 to 1.0. This may be attributed to the specific design of our liquid phase stirrer.

Data on gas-side mass transfer coefficients in stirred cell reactors are more scarce. Tamir, Merchuk, and Virkar (1979) and Yadav and Sharma (1979) investigated the influence if the diffusivity on k_g in stirred cell reactors. For $k_g \propto D_{i,g}^n$ they obtained exponents $n = 0.632$ and $0.487 - 0.518$, respectively. Our exponent of 0.5 of Sc_g is in good agreement with these data.

The reaction rate constants of this work are in reasonable agreement with the results of Schecker and Schulz (1969), see Fig. 8. However, the activation energy of the hydration, obtained here as 24.4 kJ mol^{-1} , is substantially higher compared to the value of 15.9 kJ mol^{-1} obtained by Schecker and Schultz. The agreement of Eq. (22) with the value established by Sutton and Downes (1972) is excellent.

The chemical equilibrium constant for the hydration of formaldehyde, obtained here as Eq. (24), appears to be within the range of data and relations found in the literature, see Fig. 10. A thorough comparison, however, is not possible due to considerable spreading of the literature data as mentioned before. Also, the heat of reaction, $\Delta H = -31.4 \text{ kJ mol}^{-1}$, appears to be in the wide range data, from -21.4 to $-39.4 \text{ kJ mol}^{-1}$, encountered in the literature.

5. Physical properties

Pure component properties were taken from Daubert and Danner (1985), or predicted using the methods given by Reid, Prausnitz, and Poling (1988). The distribution coefficient and diffusivity of CO_2 in water were taken from Versteeg and Van Swaaij (1988). Mixture properties were calculated using the mixing rules given by Reid et al. (1988). The density and viscosity of aqueous formaldehyde solutions were taken from Winkelman and Beenackers (2000). Diffusion coefficients in water were calculated with the Wilke-Chang method (Reid et al., 1988), where the volume of formaldehyde at its normal boiling point was taken from Daubert and Danner (1985) and that of methylene glycol was obtained with the Le Bas method (Reid et al., 1988). The distribution coefficients m_F , m_{MG} and m_W were calculated with the model of Maurer for vapour–liquid equilibria of aqueous formaldehyde solutions (Maurer, 1986; Albert et al., 2000).

6. Conclusions

The reaction rate of the hydration of formaldehyde is obtained from measuring the chemically enhanced absorption of formaldehyde gas into water in a stirred cell with a plane gas liquid interface, and mathematically modelling of the transfer processes. At the conditions prevailing in industrial formaldehyde absorbers, i.e. at temperatures of 293–333 K and at pH values between 5 and 7, the rate is found as $k_h = 2.04 \times 10^5 \times e^{-2936/T} \text{ s}^{-1}$.

Using these results, and the dehydration reaction rate constant, k_d , obtained previously at similar conditions, the chemical equilibrium constant for the hydration is obtained as $K_h = e^{3769/T - 5.494}$.

Notation

C	concentration, mol m^{-3}
D	diffusivity, $\text{m}^2 \text{ s}^{-1}$
d	stirrer diameter, m
E	liquid phase chemical enhancement factor for mass transfer, dimensionless number
J	molar flux, $\text{mol m}^{-2} \text{ s}^{-1}$

K_h	chemical equilibrium constant of the formaldehyde hydration, dimensionless number
k_g	gas phase mass transfer coefficient, m s^{-1}
k_h, k_d	reaction rate constant of hydration and dehydration, respectively, s^{-1}
k_ℓ	liquid phase mass transfer coefficient, m s^{-1}
ℓ	optical path length, m
m	molar weight, kg mol^{-1}
M	distribution coefficient (C_ℓ/C_g at equilibrium), dimensionless number
N	stirrer rate, s^{-1}
P	pressure, Pa
R	reaction rate, $\text{mol m}^{-3} \text{s}^{-1}$
Re	Reynolds number, $d^2 N \rho / \eta$, dimensionless number
S	gas liquid interfacial area, m^2
Sc	Schmidt number, $\eta / \rho D$, dimensionless number
Sh	Sherwood number, $k_g d_g / D_g$ or $k_\ell d_\ell / D_\ell$, dimensionless number
T	temperature, K
t	time, s
V	volume, m^3
v	diffusivity ratio, $D_{F,\ell} / D_{MG,\ell}$, dimensionless number
W	weight
x	distance into the liquid, m

Greek letters

δ	film thickness, m
ε	extinction coefficient, $\text{m}^2 \text{mol}^{-1}$
η	viscosity, Pa s
ρ	density, kg m^{-3}
Φ	molar transfer rate, mol s^{-1}
ϕ_R	reaction factor, dimensionless number
$\phi_{v,g}$	gas phase volumetric flow rate, $\text{m}^3 \text{s}^{-1}$

Subscripts

F	formaldehyde
g	gas phase
IF	interface
i	component i
ℓ	liquid phase
MG	methylene glycol
tot	total
W	water
$x = 0$	gas–liquid interface
$x = \delta_\ell$	interface between the liquid film and the liquid bulk

Superscripts

—	(overbar) bulk conditions
0	initial
in	feed conditions
sat	saturated

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Appendix A.

In the calculation of the hydration rate constants, the bulk liquid concentrations of formaldehyde and methylene glycol were neglected. In this appendix, we take a closer look at the influence of this assumption by modelling the system without neglecting the bulk liquid concentrations, and comparing the results to the ones previously obtained.

A.1. Model equations

During a kinetic experiment, gas flow continuously through the headspace of the stirred cell, while the liquid is in batch mode. The transient component balances over the headspace and the liquid bulk read

$$V_g \frac{d\bar{C}_{i,g}}{dt} = \phi_{v,g}^{\text{in}} C_{i,g}^{\text{in}} - \phi_{v,g} \bar{C}_{i,g} - S(J_i)_{x=0} \quad (i = F, MG, W), \quad (\text{A.1})$$

$$V_\ell \frac{d\bar{C}_{i,\ell}}{dt} = n_i V_\ell R_F + S(J_i)_{x=\delta} \quad (i = F, MG) \quad (\text{A.2})$$

with the initial conditions

$$t = 0, \quad \bar{C}_{F,g} = \bar{C}_{MG,g} = \bar{C}_{F,\ell} = \bar{C}_{MG,\ell} = 0, \quad \bar{C}_{W,g} = C_{W,g}^{\text{sat}}. \quad (\text{A.3})$$

In Eqs. (A.1) and (A.2), x denotes the distance into the liquid, thus $(J)_{x=0}$ denotes the flux of a component at the gas–liquid interface and $(J)_{x=\delta}$ denotes the flux into the liquid bulk at the interface of the liquid film and bulk, R_F is the rate of the hydration reaction in the liquid bulk, see Eq. (14), and the stoichiometric coefficients, n_i , are given by $n_F = -1$ and $n_{MG} = 1$.

The rate constant k_h was determined for each experiment by adjusting it until $\bar{C}_{F,g}$, obtained by integration of Eqs. (A.1)–(A.3) over the experimental run time, was equal to its measured value.

The Fourier times for diffusion in the gas and liquid film (typically of the order of 0.1 s) are much smaller than the time scale at which variation of the bulk concentrations

take place (the gas phase residence time was of the order of 10–20 s). Therefore, during the integration, the fluxes of formaldehyde and methylene glycol at the interface are calculated by solving simultaneously Eqs. (16)–(18) and the expression for the enhancement factor of formaldehyde, which reads in this case (Winkelman & Beenackers, 1993)

$$E_F = 1 + \frac{\left[1 - \frac{\tanh[\phi_R]}{\phi_R}\right] \left[K_h - \frac{C_{MG,\ell,IF} - \bar{C}_{MG,\ell}}{C_{F,\ell,IF} - \bar{C}_{F,\ell}}\right] + \left[\frac{K_h \bar{C}_{F,\ell} - \bar{C}_{MG,\ell}}{C_{F,\ell,IF} - \bar{C}_{F,\ell}}\right] \left[1 - \frac{1}{\cosh[\phi_R]}\right]}{(K_h + v) \frac{\tanh[\phi_R]}{\phi_R}}, \quad (\text{A.4})$$

where ϕ_R is given by Eq. (22).

The fluxes from the liquid film into the liquid bulk are obtained from the analytical expressions for the concentrations in the film (Winkelman & Beenackers, 1993) by differentiation according to $(J_i)_{x=\delta} = -D_{i,\ell}(\mathrm{d}C_i/\mathrm{d}x)_{x=\delta}$, giving

$$\begin{aligned} (J_F)_{x=\delta} &= (J_F)_{x=0} - k_{\ell,F} \\ &\times \frac{K_h(C_{F,\ell,IF} + \bar{C}_{F,\ell}) - (C_{MG,\ell,IF} + \bar{C}_{MG,\ell})}{(K_h + v) \frac{\tanh[\phi_R]}{\phi_R}} \\ &\times \left(1 - \frac{1}{\cosh[\phi_R]}\right) \end{aligned} \quad (\text{A.5})$$

and

$$\begin{aligned} (J_{MG})_{x=\delta} &= -(J_F)_{x=\delta} + k_{\ell,F} \\ &\times \left[C_{F,\ell,IF} - \bar{C}_{F,\ell} + \frac{C_{MG,\ell,IF} - \bar{C}_{MG,\ell}}{v}\right]. \end{aligned} \quad (\text{A.6})$$

A.2. Results

The transient model described above was solved numerically for k_h for each experiment. When compared to the k_h data obtained Eqs. (15)–(18) and (21), the differences were small. On an average, the rates obtained here were 0.48% larger, with a maximum of 1.02%. Since this is well within the estimated experimental uncertainty, we conclude that the influence of the bulk concentration of formaldehyde and methylene glycol can safely be neglected in the evaluation of the experiments.

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